



Ottawa Hull K1A 0C9

(21)	(A1)	2,154,818
(22)		1995/07/27
(43)		1996/02/07

(51) Int.Cl. <sup>6</sup> C09D 133/06; D06M 11/32; D06M 15/263

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Pigment Concentrate and Its Use**

(72) Bergfried, Stefan - Germany (Federal Republic of) ;  
Sawitowski, Thomas - Germany (Federal Republic of) ;  
Silber, Stefan - Germany (Federal Republic of) ;  
Vallerien, Sven-Uwe - Germany (Federal Republic of) ;

(71) Th. Goldschmidt AG - Germany (Federal Republic of) ;

(30) (DE) P 44 27 931.0 1994/08/06

(57) 2 Claims

**Notice:** This application is as filed and may therefore contain an incomplete specification.



**THIS PAGE BLANK (USPTO)**

The invention relates to an aqueous concentrate of an electrically conductive, ultrafine pigment and an antistatic finish for synthetic materials, films, sheets, synthetic fibers and laminated papers comprising an effective amount of the inventive pigment concentrate.

Electrically conductive pigments and fillers are used to produce antistatic coatings. A plurality of such materials is described in the literature. The following patent publications are named as examples: DE-A-43 03  
10 385, EP-A-0 582 371, WO 92/01631, EP-A-0 459 552, EP-A-0 415 477 and EP-A-0 448 946.

These pigments differ in their chemical composition and also in their morphology. In particular, particle size and shape play an important role. A prerequisite for achieving a uniform surface conductivity for coatings prepared with such pigments is the formation of uniform conductive strips resulting from the contact of the pigment particles with one another (percolation). The formation of such electrically conductive paths sets in  
20 at a pigment volume concentration (PVC) at which the electrical resistance decreases drastically and frequently by several orders of magnitude. This threshold concentration is referred to in the literature as the percolation PVC (for example, J. Composite Materials, 26, 2727, (1992)).

It is well known that the percolation PVC of non-aqueous coatings can be lowered, if the pigment is caused to flocculate in a controlled manner so that net-like and tape-like structures of contacting particles result  
30 (Farbe + Lack, 100, 171, (1994)).

The inventive problem now arises of preparing vehicle-free, aqueous pigment compositions, preferably in the form of a paste or concentrate.

An object of the present invention is an aqueous concentrate of an electrically conductive, ultrafine pigment.

Another object of the invention is an anti-static finish for synthetic materials, films, sheets, synthetic fibers and laminated papers comprising an effective amount of the inventive pigment concentrate.

These compositions are universally useable with respect to their dispersability in different vehicles, such as polyvinyl chloride, polyvinyl acetate, polyester, polyacrylate, polyurethane or also in copolymers or mixtures of these. At the same time, flowable concentrates with a high pigment content are to be prepared, the further processing of which is problem-free. For example, the stability of these pastes should be high, vehicle or dilution shock should be avoided and, in particular, a controlled flocculation should be attained without additional additives in order to ensure a sufficiently high electrical conductivity.

Typical dispersing additives for aqueous systems are surface active, anionic, cationic or nonionic substances, which have a low molecular weight. For example, it is known that sodium phosphate, sodium sulfonate, sodium oleate or sodium stearate is used to improve the dispersability of electrically conductive doped tin(IV) oxide (JP 162184180). The use of polyacrylates of low molecular weight as dispersants for pigments in aqueous coating is also known. In US patent 3,980,602, dispersing additives are described, which contain 5 to 25% by weight of acrylic acid or methacrylic acid in polymers, which are synthesized from alkyl acrylates and styrene or certain alkyl methacrylates.

However, adequate stabilization of the aqueous pigment concentrates cannot be achieved according to this state of the art.

Surprisingly, the aforementioned requirements are satisfied by an aqueous pigment concentrate, which consists of

- |    |            |  |
|----|------------|--|
|    | 40 - 60%   | of an electrically conductive pigment based on metal oxides with a specific powder resistance of 0.3 to $10^6$ ohm x m and a particle size of 10 nm to 50 $\mu$ m, |
|    | 2 - 4.9%   | of a terpolymeric, anionic polyacrylate consisting of  |
| 10 | 35 - 45%   | of an alkyl (meth)acrylate with 1 to 3 carbon atoms in the alkyl chain,  |
|    | 35 - 45%   | of an alkyl (meth)acrylate with 4 to 12 carbon atoms in the alkyl chain and  |
|    | 10 - 30%   | of acrylic acid or methacrylic acid,   |
|    | 0.1-4.9%   | of an amine, so that a pH of 7.0 to 10.0 results,  |
| 20 | 0.1-0.9%   | of a nonionic, surface active addition product of ethylene oxide and an alkylphenol, an alcohol or a carboxylic acid,  |
|    | 0 - 2.0%   | of a thickener based on a polyacrylate, a polyurethane or a cellulose derivative,  |
|    | 0 - 6.0%   | of a glycol derivative as well as  |
|    | 21.3-57.8% | of water.  |

As a preferred electrically conductive pigment, tin(IV) oxide, doped with antimony and/or fluorine, which optionally is coated onto a supporting pigment (rutile, barium sulfate, mica, etc.), for example, is utilized.

As alkyl (meth)acrylate copolymer with 1 to 3 or 4 to 12 carbon atoms in the alkyl chain, particularly methyl methacrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, isodecyl methacrylate and stearyl methacrylate are utilized.

The following can be used as amine component:  
ammonia, diethylethanolamine, ethanolamine,  
diethanolamine, triethanolamine, monoisopropanolamine,  
triethylamine, monoethanolamine, aminomethylpropanol,  
10 diethylamine, morpholine, dimethylethanolamine.

Butyl glycol, for example, is suitable as the glycol derivative.

The pigment concentrate is prepared in a typical dispersing process. Shear forces must be able to act in order to divide pigment agglomerates. These forces can be generated in a plurality of different machines (dissolvers, ball mills, sand mills, etc.), the transfer of shear energy to the pigment particles being affected but little by the addition of additives. It is, however,  
20 important that the newly created surfaces are wetted rapidly in order to prevent agglomerates being formed once again.

It is now vital that the fine distribution of the pigment particles in the dispersion, which is achieved by the dispersing, be stabilized, as far as possible, up to the dry film. In aqueous media, the stabilization is dominated by electrical charges, if the individual solid particles have the same type of charge. Steric stabilizing terms also play a role as the film dries out.

30 The addition of glycols causes a decrease in the drying rate and, with that, an increase in the processing time and moreover improves the flow. The thickener is added in order to increase the viscosity of the pigment paste after the milling and to modify the rheological behavior of this paste.

The inventive pigment concentrate is outstandingly suitable for antistatic finishes for synthetic materials, films, sheets, synthetic fibers and laminated papers.

The inventive pigment paste has a surprisingly high stability. This causes several important technical improvements. For example, the problem-free dilutability permits the selective adjustment of the viscosity to values suitable for the respective processing process. Industrial application by machine under constant  
10 conditions is thus assured over a prolonged period. For example, the coating can be accomplished by a spraying process or in an immersion bath. As a result of this increased stability, prolonged standing times and/or breakdown times are also acceptable. For preparing this coating, the inventive pigment concentrate can be dispersed in different water-based vehicles, such as PVC, polyvinyl acetate, polyester, polyurethane or polyacetate, or also in copolymers and/or mixtures of these without a vehicle. A further technical advantage  
20 consists therein that for the above-mentioned dispersing process, generally no additional defoamer is required. It is, however, of decisive importance for the industrial utilization of the coating for antistatic finishes on synthetic materials, synthetic fibers, films, sheets and laminated papers that a controlled flocculation while the film is drying becomes possible without the need for additional additives to the coating system.

The inventive concentrate formulation and its use is described in greater detail in the Examples below (it is  
30 understood that these Examples are provided by way of illustration and not by way of limitation):

The components of the formulations are as follows:

1. Terpolymers:      1.    45% butyl methacrylate, 30%  
   methyl methacrylate and 25%  
   acrylic acid,

2. 10% styrene, 70% methyl methacrylate and 20% acrylic acid (comparison substance),
  3. 45% butyl methacrylate, 45% methacrylate and 10% acrylic acid,
- all as a 50% solution in butyl glycol.

10

## 2. Ethylene oxide

- addition products:
1. Castor oil ethoxylate
  2. Ethoxylate of sorbitol monolaurate
  3. Ethoxylate of sorbitol hexanoleate

## 3. Nitrogen compounds: 1. Ammonia

2. Dimethylethanolamine

20 3. 2-Amino-2-methyl-1-propanol

## 4. Thickener:

1. Polyacrylate

2. Cellulose

The types given in the Table refer to the above listing of the components; the concentration by weight is given in every case. The stability of a 1 to 20 dilution of the inventive pigments in fully deionized water (absence of a deposit) is considered.

30 The electrically conductive, fluorine doped tin(IV) oxide has an average particle size of 0.2  $\mu\text{m}$ , with an upper particle size limit of 2 mm. The specific powder



2154818

resistance is 10 ohm x m, and the bulk density is 0.35 g/mL. The BET surface area is between 50 and 60 m<sup>2</sup>/g.

Form- ulation	Content of SnO <sub>2</sub>	Terpolymer (50% in Butyl Glycol)	Amine	Thickener	EO- Addition Product	H <sub>2</sub> O	Stability without Additive	Stability with Additive
1	40%	5% type 2	1.8% type 3	0.5% type 2	0.9% type 3	51.8%	5 min.	< 1 hour sediment
2	42%	8% type 1	1.2% type 2	0.8% type 1	0.8% type 2	47.2%	5 min.	after 5 h slight sediment
3	45%	7.5% type 2	4.0% type 2	1.2% type 1	0.3% type 2	42.0%	4 min.	after 30 min. distinct sediment
4	50%	10% type 3	0.5% type 1	1.6% type 2	0.4% type 1	37.5%	4 min.	only after 10 h slight sediment
5	54%	10% type 1	2.0% type 2	1.0% type 1	0.9% type 2	32.1%	4 min.	after 10 h no sediment
6	60%	10% type 2	4.5% type 3	0.5% type 2	0.6% type 3	24.4%	4 min.	after 1 h distinct sediment

The Table shows that the stability of the diluted, inventive pigment concentrates 2, 4, and 5 is clearly higher than that of the Comparison Examples 1, 3 and 6.

**THIS PAGE BLANK (USPTO).**

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:-

1. A pigment concentrate consisting of
  - 40 - 60% of an electrically conductive pigment based on metal oxides with a specific powder resistance of 0.3 to  $10^6$  ohm x m and a particle size of 10 nm to 50  $\mu$ m,
  - 2 - 4.9% of a terpolymeric, anionic polyacrylate consisting of
    - 10 35 - 45% of an alkyl (meth)acrylate with 1 to 3 carbon atoms in the alkyl chain,
    - 35 - 45% of an alkyl (meth)acrylate with 4 to 12 carbon atoms in the alkyl chain and
    - 10 - 30% of acrylic acid or methacrylic acid,
    - 0.1-4.9% of an amine, so that a pH of 7.0 to 10.0 results,
    - 20 0.1-0.9% of a nonionic, surface active addition product of ethylene oxide and an alkylphenol, an alcohol or a carboxylic acid,
    - 0 - 2.0% of a thickener based on a polyacrylate, a polyurethane or a cellulose derivative,
    - 0 - 6.0% of a glycol derivative as well as
    - 21.3-57.8% of water.
2. An antistatic finish for synthetic materials, films, sheets, synthetic fibers and laminated papers comprising
  - 30 an effective amount of the pigment concentrate of claim 1.



## ABSTRACT OF THE DISCLOSURE

A pigment concentrate is prepared consisting of

- 40 - 60% of an electrically conductive pigment based on metal oxides,
- 2 - 4.9% of a terpolymeric, anionic polyacrylate
- 0.1-4.9% of an amine, so that a pH of 7.0 to 10.0 results,
- 0.1-0.9% of a nonionic, surface active addition product of ethylene oxide and an alkylphenol, an alcohol or a carboxylic acid,
- 0 - 2.0% of a thickener based on a polyacrylate, a polyurethane or a cellulose derivative,
- 0 - 6.0% of a glycol derivative as well as
- 21.3-57.8% of water.

**THIS PAGE BLANK (USPTO;**